Pertanika J. Sci. & Technol. Supplement 9(1): 1 - 9 (2001)
ISSN: 0128-7680

Kinetic Studies on the Adsorption of Sungai Sireh Raw Water's Natural Organic Matters

Ahmad Jusoh[1], Megat Johari Megat Mohd Noor[2] & See Boon Piow[2]
[1]Universiti Putra Malaysia Terengganu
[2]Department of Civil Engineering, Universiti Putra Malaysia
43400 UPM, Serdang, Selangor

ABSTRACT

The presence of dissolved organics in potable water supply is aesthetically undesirable. Apart from imparting colour, taste and odour to treated water, it is also potentially hazardous to health. Two types of coconut shell derived activated carbon, KI-6070 and KI-8085, provided by *Kekwa Indah Sdn Bhd,* were studied for the removal of dissolved organic compounds from Sungai Sireh Water Treatment Plant raw water, notorious of its high organic content. The respective external surface area of the KI-6070 and KI-8085 are approximately 277 m^2/g and 547 m^2/g.

The rate constant (K_1) for the KI-8085 was higher than that of the KI-6070, ranging between 30 and 70 %, for adsorbent dosages between 1.0 and 3.0 g. This was expected since the total surface area (specific and external surface areas) of the KI-8085 was higher than that of the KI-6070. The rate constant for the mass transfer was a function of the adsorbent dosage where both adsorbents indicated a proportional increase in the rate constant with increasing adsorbent dosage. The increasing dosage raised the intraparticle diffusion rate constant (K_{id}) for both the KI-6070 and KI-8085, with the KI-8085 having a higher intraparticle diffusion rate.

Keywords: Kinetic, adsorption, natural organic matter, granular activated carbon

INTRODUCTION

Conventional treatment processes are not sufficiently efficient in removing dissolved organic carbon (DOC) in water. Water containing high organic matter requires greater dosage of chlorination at the disinfection stage and consequently increases the formation trihalomethanes (THMs) in the treated water. This indirectly increases the cost of processing water. Higher THMs concentration in the water also poses a health hazard to consumers.

Recently, activated carbon has been identified as the most suitable and economical way to the removal of selected organic compounds. A thorough understanding of the adsorption and diffusion qualities of these humic substances is required, as macromolecular organic matter is ubiquitous in the aqueous environment (Summers and Roberts 1988).

The rate of adsorption can be categorised to several steps as follows:

- Transport of solute from bulk solution phase to the boundary layer or surface film surrounding the adsorbent particle.
- Transport of solute across the boundary layer to the exterior surface of the adsorbent particle.
- Diffusion of solute within these pores, from the exterior of the particle to the interior surfaces of the particle.
- The physical or chemical binding of adsorbate to the internal surface of the adsorbent.

In water treatment, the steps of bulk transport and chemical or physical bonding are generally rapid, a either film diffusion or pore diffusion or both control the overall rate of adsorption.

NOM Removal Kinetics

The resolved mass transfer equation is as follows:

$$\frac{dC_1}{dt} = K_L a[C_e - C_t] \quad (1)$$

The equation can be resolved under the following boundary conditions:

$$C = C_o \text{ for } t = 0 \text{ and } C = C_e \text{ for } t \rightarrow \infty$$

And the solution of this equation is similar to the Lagergren's mass transfer equation as shown in the equation below (Namasivayam and Yamuna 1995 ; Low *et al.* 1996):

$$\log(q - q_t) = \log\ q - \frac{K_L a}{2.303} t \quad (2)$$

In order to calculate virtual initial concentration Co', the Lagergren's mass transfer equations can be modified by introducing an 9 to the logarithmic equation as shown in equation (3) and (4).

$$\text{In}\frac{C_e - C_t}{C_e - C_o} = \alpha - K_L a t \quad (3)$$

$$\frac{C_e - C_t}{C_e - C_o}\frac{1}{e^{\alpha}} = \frac{C_e - C_t}{C_e - C_o} \quad (4)$$

Intraparticle Diffusion

The rate for intraparticle diffusion (Kid) is given by Weber and Morris (Namasivayam and Yamuna 1995) as

$$q = K_{id}\ t^{0.5} \quad (5)$$

The kinetics adsorption study by Namasivayam and Yamuna (1995) show that the linear portions of the curves do not pass through the origin indicating that intraparticle diffusion is not the only rate limiting control in the adsorption of dye on biogas residual slurry.

Empirical Model

In order to estimate the rate removal of adsorbate from effluent by an adsorbent, the following empirical mathematical model has been developed between contact time for the adsorption of adsorbate (Prakash *et al.* 1987):

$$\log(t+1) = K(C_i - C_t)^A \quad (6)$$

$$\log(C_i - C_t)\frac{1}{A}\log[\log(t+1)] - \frac{1}{A}\log\ K \quad (7)$$

MATERIALS AND METHODS

Preparation of GAC

The GAC used in this study is manufactured by KEKWA INDAH SDN BHD in Nilai. Two types of activated carbons made from coconut shell were used in this study (KI-6070 and KI-8085) and the characteristics of both activated carbons supplied by the manufacturer are given in Table 1.

TABLE 1
Characteristics of the activated carbon

Grade	Iodine No. mg/g	CTC (%)	Bulk Density G/cm^3	Ash (%)
KI-6070	1200 – 1300	60 – 70	0.47 – 0.51	3.0 – 4.0
KI-8085	1300 – 1400	70 – 80	0.40 – 0.44	3.0 – 4.0

The information given in Table 1 does not show the specific surface area, characteristics of the pore size distribution and type of pore volume (micropore, mesopore and macropore) available in the activated carbons though being important in the adsorption process (Lambert and Graham 1995; Kameya *et al.* 1997). Hence, an additional test (Brunauer, Emmett and Teller (BET) method) is required to characterize the physical properties of the adsorbents used in study.

The GAC used in this experiment was thoroughly washed with hydrochloric acid 1.0 M and rinsed before boiling with distilled water. This is to remove the unknown impurities, which will affect the adsorption of the activated carbon (Summers and Roberts 1988; Srivastana and Tyagi 1995). The GAC was soaked in distilled water for 24 hours and heated in an oven at 105°C for 2 days (Peel and Benedek 1980; Cooney and Xi 1994). Finally the porosity and specific gravity of the GAC were determined. The GAC was stored in dessicator until required.

Batch Experiment

All tests were carried out at room temperature and distilled water was used for cleaning off the apparatus control samples were simultaneously carried out to ensure sorption was done by activated carbon and not by the wall of the container.

The GACs (KI-6070 and KI-8085) used in the study were supplied by KEKWA in 20x50 mesh size (0.3-0.84 mm U.S Standard). Wetted GAC was ground with mortar and pestle to pass a 300 mm sieve mesh. This was done since smaller particle will achieve an equilibrium stage faster as compared to large particle size and therefore, it can reduce the experimental time required (David *et al.* 1983; Snoeyink 1991). Normally for batch studies, the adsorbent material was powdered and sieved to 200-250 mesh particle size (Srivastana and Tyagi 1995). The resulting powdered carbons were dried at 103°C for 24 hours and stored until for further use.

Time Course Study

Sample of activated carbon (KI-6070 and KI-8085) in the particle size of less than 300 mm were mixed with filtered (0.45 mm filter paper) raw water at 150 rpm where the NOM concentration was predetermined at a volume of 400ml for 3 days. The pH was adjusted to pH 5.0 using mild hydrochloric acid (pH 4) for the batch experiment. Each

solution (4 ml) in the batch reactor was removed after the predetermined contact time; the reaction mixture was then filtered with 0.45 mm filter paper again and the filtrate was analyzed for COD and DOC. Both activated carbons reached an equilibrium stage at about 6 hours.

Kinetic Study

The various quantities of adsorbents (KI-6070 and KI- 8085) ranging from 1.0 to 3.0 g was added to a 400 ml of predetermined NOM concentration of water samples. The mixture was mixed at 150 rpm. The sample of carbon was introduced to the reaction flask at time zero and then 4 ml of the solution was withdrawn at various intervals of time. This solution was filtered with 0.45 mm of filter paper to remove particulates and the solution was analyzed for DOC.

Aqueous Solutions

The raw water was taken from the intake point of the Sungai Sireh Water Treatment Plant. This plant receives a highly coloured (450 TCU) raw water, typical of swampy and peaty waters, containing material normally attributed by the humic and formic acid . The concentration of natural organic matter in the raw water was measured directly in terms of DOC using TOC analyzer.

RESULTS AND DISCUSSION

Characteristics of Activated Carbon

The physical characteristics of activated carbon are very important in determining the capacity and feasibility of the activated carbon to adsorb certain substances in terms of physical aspects. The surface and pore characteristics of the activated carbon samples (KI-6070 and KI-8085) as measured by BET method are given in Table 2. It was found that the specific surface area of KI-8085 is about 20% higher than that of KI-6070. Hence, we can conclude that the extra 20% surface area of KI-8085 was mainly attributed to the external surface area of the activated carbon itself.

It is also observed that both types of activated carbon have approximately the same mean pore radius of about 14Å. This pore radius is in the micropores region of less than 20Å (Cheremisinoff 1993).

After the experiment, it was found that KI-8085 has a higher adsorption capacity compared to KI-6070, this is mainly caused by "molecular sieves" mechanism which is influenced by the changes in the size and shape of the macromolecule (Brasquet *et al.* 1997; Newcombe *et al.* 1997b). Size exclusion of this molecular sieves effect is obvious, when the capacity of the adsorbent increases with increasing external surface area

TABLE 2
Structural characteristics of the adsorbents

Parameter	KI-6070	KI-8085
BET surface area (m^2/g)	1053	1266
Langmuir surface area (m^2/g)	1402	1705
External surface area (m^2/g)	277	547
Micropore volume (cm^3/g)	0.362	0.334
Mean pore radius (Å)	14.6	14.4

(mesopore size) of the adsorbent (Brasquet *et al.* 1997). As the pores size increases, it will allow more dissolved organic matters and also bigger molecular size of solutes to gain access to the micropores area where most of the adsorption processes are taking place (Cheremisinoff 1993; Brasquet *et al.* 1997; Newcombe *et al.* 1997a).

Time Course Study

The sorption of NOM as a function of contact time for various dosages of adsorbents, KI-6070 and KI-8085, ranging from 1.0 g to 3.0 g is shown in Figs. 1 and 2. The fractional sorption of organic matters by both the activated carbons increases as the dosage of adsorbent increased. Fast sorption occurred during the first 80 minutes and the equilibrium was achieved after 150 minutes for all dosages studied as indicated in both figures.

NOM Removal Kinetics

The time course studies showed sorption to be a rapid phenomenon as illustrated in Figs. 1 and 2. The resolved mass transfer equations (1) and (2) were used to estimate the rate constant of the adsorption (Table 3). These results demonstrated that the ordinate interception was not negligible and that double mechanism would have occurred; first an instantaneous sorption, inducing a rapid decrease in initial concentration (C_o) to a virtual initial concentration C_o', followed by a sorption occurring at a rate given by the slope of the linear plots (Guibal *et al.* 1995). Hence Lagergren's mass is not valid to illustrate, this condition and the equation can be modified by introducing an α component to the logarithmic equation (3) which yields the equation (4), to allow C_o to be estimated as shown in Table 3.

The value of α can be determined from the interception of the linear plot of equation (3). The result of the kinetics data and mass transfer coefficient as a function of the dosage are shown in Table 3.

The rate constant (K_L) for KI-8085 were higher than that of KI-6070, ranging from 30 to 70 %, due to the specific surface area and external surface area of KI-8085 being higher than that of KI-6070. This is because KI-8085 provides more surface area and bigger pore sizes which facilitates the adsorption of NOM with larger molecular size

TABLE 3
Determination of rate constant of NOM Removal Kinetics

Adsor -bent	Dose g	C_e,mg/l	C_o',mg/ l	α	K_L,min^{-1}	R2
KI-	1.0	20.601	30.924	-0.041	1.70×10^{-2}	0.992
6070	1.5	17.857	32.005	0.047	1.80×10^{-2}	0.998
	2.0	16.102	32.106	0.048	1.76×10^{-2}	0.997
	2.5	12.860	33.686	0.125	2.11×10^{-2}	0.995
	3.0	12.386	28.105	-0.188	2.03×10^{-2}	0.994
KI-	1.0	16.394	26.415	-0.045	2.48×10^{-2}	0.995
8085	1.5	13.438	26.285	-0.045	2.34×10^{-2}	0.965
	2.0	10.213	30.063	0.175	3.09×10^{-2}	0.988
	2.5	7.525	30.646	0.178	2.79×10^{-2}	0.997
	3.0	5.106	27.449	0.026	2.20×10^{-2}	0.994

Note: Initial concentrations of sample were 31.3576 and 26.87 mg/l for KI-6070 and KI-8085 respectively

(Cornel *et al.* 1985; Brasquet *et al.* 1997). External surface area (mesopore) was found to be more important for the mass transfer coefficient of the adsorption process. A study by Newcombe *et al.* (1997b) also showed that mesopores volume in activated carbon had a greater effect on the adsorption of NOM.

The rate constant of the mass transfer is also a function of adsorbent dosage. Both adsorbents (KI-6070 and KI-8085) how that the rate constant of the adsorbents increased proportionally with an increase in adsorbent dosage. As the dosage of activated carbon increases, it provides greater surface area for adsorption to take place, as compared to lower dosage of adsorbents.

The virtual initial concentration C_o', in both equation (3) and (4) is the concentration of the solution, where the adsorption process follows the first order kinetic reaction. The estimation of virtual concentration for both adsorbents (KI-6070 and KI-8085) was slightly higher than initial concentrations for most cases studied (Table 3). The instantaneous removal of the adsorbate was not significant in the study, because the concentrations of the NOM used in the study were able to give a constant rate of the adsorption process.

Intraparticle Diffusion

The adsorption of the NOM took place in two phases (Figs. 1 and 2). The first phase of solute uptake, the 'immediate solute uptake,' which was achieved within a few minutes was followed by the subsequent uptake of solute; the latter phase continued for a longer period of time. The contact-time experimental results can be used to study the rate limiting step in the adsorption process. Since the particles were vigorously agitated during the adsorption period, it is reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. Therefore, the rate limiting step may be film or intraparticle diffusion.

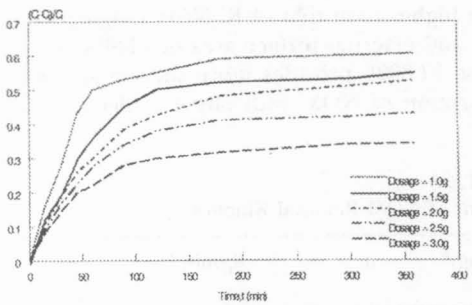

Fig. 1: Time course study of the actived carbon KI-6070 or removing of NOM. Conditions: 400ml of 31.356mg/l of NOM with different amounts of activated carbon

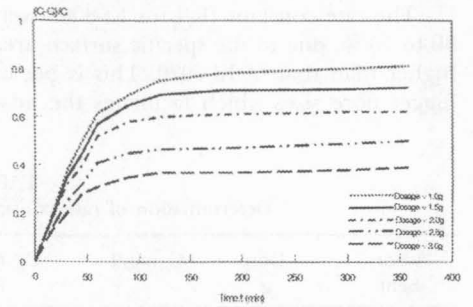

Fig. 2: Time course study of the activated carbon KI-8085 for removing of NOM. Conditions: 400ml of 31.356mg/l of NOM with different amounts of activated carbon

From the rate constant for intraparticle diffusion of equation (5), the plots of q versus $t^{0.5}$ are shown in Figs. 3 and 4. All plots have the same general features. The initial curved portion is attributed to the bulk diffusion effect, the linear portion to the intraparticle diffusion effect and the plateau to the equilibrium. The linear portions of the curves do not pass through the origin indicating that intraparticle diffusion is not the only rate controlling step for the adsorption of NOM onto adsorbents used in the study. Kid values obtained from the slope linear portions of the curves at each different

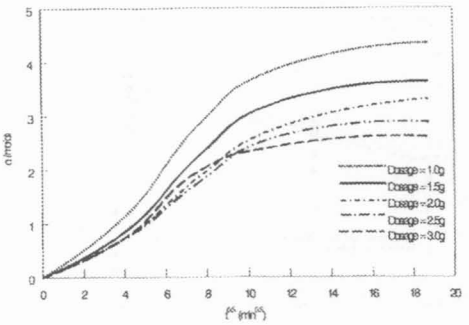

Fig. 3: Plots of NOM adsorbed versus t 0.5 for different adsorbent (KI-6070) dosages

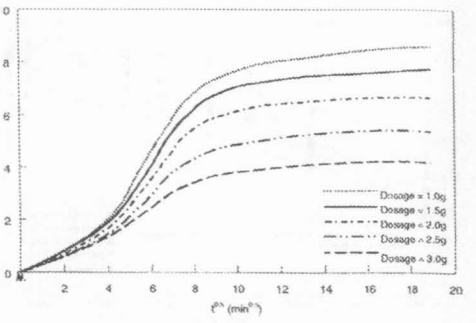

Fig. 4:Plots of NOM adsorbed versus t 0.5 for different adsorbent (KI-8085) dosages

dosage of adsorbents are shown in Table 4. The results generally show that increasing adsorbent dosage increased the intraparticle diffusion rate constant for both KI-6070 and KI-8085. KI-8085 gave a higher intraparticle diffusion rate compared to KI-6070 at each different dosage of adsorbents.

TABLE 4
Kinetic constant of adsorption for KI-6070 and KI-8085

Dose, g	KI-6070		KI-8085	
	K_{id}	R^2	K_{id}	R^2
1.0	0.2322	0.8789	0.3805	0.9283
1.5	0.2766	0.9854	0.5182	0.9195
2.0	0.2829	0.9916	0.6689	0.9318
2.5	0.3397	0.9919	0.7960	0.9478
3.0	0.3858	0.9786	0.8568	0.9458

Higher K_{id} indicates an enhancement in the rate adsorption. The adsorption capacity for KI-8085 was higher than that of KI-6070 for the same dosage of activated carbon.

Empirical Model

To estimate the rate of removal of NOM from water by different dosages of activated carbon, the empirical model of equations (6) and (7) were used. The values of K and A were reported depending on influent concentration, C_i the density and particle size of the adsorbent. The values of K and A were determined from the plots of log $(C_i - C_t)$ versus log (log(t + 1)) (Figs. 5 and 6). The straight lines thus obtained indicate the applicability of the model to the present study.

The relationships between dosage and the adsorbate removal rates for both activated carbons, KI-6070 and KI-8085, are presented in Table 5. It is clear that the removal of NOM in water can be computed at various time or a given dosage of adsorbent.

CONCLUSIONS

Activated carbons namely KI-6070 and KI-8085 were used in the study to adsorb NOM. Generally, KI-8085 performed better compared to KI-6070. This is mainly due to its

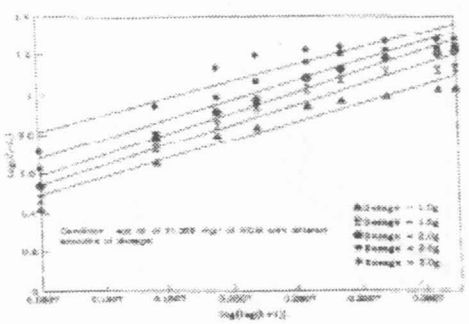

Fig. 5

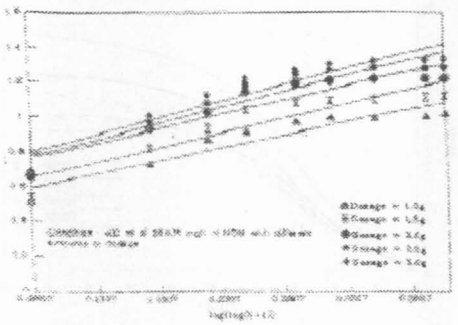

Fig. 6

TABLE 5
The empirical model for KI-6070 and KI-8085

Adsorbent	Dose, g	Empirical Model	R^2
KI-6070	1.0	Log(t+1)=0.6495(Ci-Ct)0.5462	0.9413
	1.5	Log(t+1)=0.6472(Ci-Ct)0.4961	0.9424
	2.0	Log(t+1)=0.6303(Ci-Ct)0.4770	0.9671
	2.5	Log(t+1)=0.5405(Ci-Ct)0.5129	0.9268
	3.0	Log(t+1)=0.3888(Ci-Ct)0.6027	0.8602
KI-8085 1.0	1.5	Log(t+1)=04748(Ci-Ct)0.6725	0.8677
	2.0	Log(t+1)=0.4898(Ci-Ct)0.5949	0.8610
	2.5	Log(t+1)=0.4116(Ci-Ct)0.6063	0.8565
	3.0	Log(t+1)=0.4489(Ci-Ct)0.5477	0.8645
		Log(t+1)=0.4485(Ci-Ct)0.5304	0.8783

higher specific surface area and a greater percentage of mesopores, which allows greater accessibility of macroorganic to the internal pores.

The rate constant (KL) for KI-8085 were higher than that of KI-6070, ranging from 30 to 70 %, due to the specific surface area and external surface area of KI-8085 being higher than that of KI-6070. External surface (mesopores) was found to be more important for the mass transfer coefficient of the adsorption process. The rate of the mass transfer is also a function of adsorbent dosage. Both adsorbents (KI-6070 and KI-8085) showed that the rate constant of the increased proportionally with increasing adsorbent dosage.

NOTATION

a	Specific surface area
A,K	Empirical Constant
C_e	Equilibrium Concentration
C_i	Influent Concentration
C_o,C_t	Concentration at time zero and at time t
q	Unit mass of adsorbate/mass of adsorbent
q_t	Amount of adsorbate adsorbed at time t
K_{id}	A constant that depicts rate factor

K_L Rate constant of adsorption
t Time

REFERENCES

BRASQUET, C., E. SUBRENAT and P. Le CLOIREC. 1997. Selective adsorption on fibrous activated carbon of organics from aqueous solution: correlation between adsorption and molecular structure. *Wet Sci. Tech* **35(7)**: 251-259.

CHEREMISINOFF, N. P. 1993. *Carbon Adsorption for Pollution Control.* Pp 50-57. Engleweed Cliffs, New Jersey: PTR Prentice Hall.

COONEY, D. O and Z. XI. 1994. Activated carbon catalyzed reactions of phenolics during liquid-phase adsorption. *J. AICHE* **40(2)**: 361-364.

CORNEL, P. K., R. S. SUMMERS and P. V. ROBETS. 1985. Diffusion of humic acid in dilute aqueous solution. *J. Colloid Interface Sci.* **110**: 149-164.

DAVID, W. H., J. C. CRITTENDEN, M. ASCE and W. E. THACKER. 1983). User-oriented batch reactor solutions to the homogeneous surface diffusion model. *J. Environ. Eng.* **109**: 83-101.

GUIBAL, E., R. LORENZELLI, T. VINCENT and P.L. CLOIREC. 1995. Application of silica gel to metal ion sorption: static and dynamic removal of uranyl ions. *Environ. Technol.* **16**: 101-114.

KAMEYA, T., T. HADA and K. URANO. 1997. Changes of adsorption capacity and pore distribution of biological actived carbon on advanced water treatment. *Wet. Sci. Tech.* **35**: 155-162.

LAMBERT, S. D and N. J. D. GRAHAM. 1995. Removal of non-specific dissolved organic matter from upland potable water supplies-I. Adsorption. *Wat. Res.* **29**: 2421-2426.

LOW, K.S., C. K. LEE and A. M. WONG. 1996. Carbonized spent blenching earth as a sorbent for some organic dyes. *J. Environ. Sci. Health* **31(3)**: 673-685.

NAMASIVAYAM, C and R. T. YAMUNA. 1995. Adsorption of direct red 12B by biogas residual slurry: equilibrium and rate processes. *Environmental Pollution* **89**: 1-7.

NEWCOMBE, G., M. DRIKAS., S. ASSEMI and R. BECLATT. 1997a. Influence of characterised natural organic adsorption: 1. Characterisation of concentrated reservoir water. *Wat. Res.* **31(5)** : 965-972.

NEWCOMBE, G., D. MARY and H. ROB. 1997b. Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. *Wat. Sci.* **31(5)**: 1065-1073.

PEEL, R. G and A. BENEDEK. 1980. Attainment of equilibrium in activated carbon isotherm studies. *Environ. Sci. Technol.* **3**: 66-71.

PRAKASH,O., I. MEHROTRA and P. KUMAR. 1987. Removal of cadmium from water by water hyacinth. *J. Environ. Eng.* **113(2)**: 352-365.

SNOEYINK, V.L. 1991. Adsorption of Organic Compounds. In *Water Quality and Treatment.* A Handbook of Community Water Supply, p. 782. ed. W.P. Frederick. McGraw Hill. New York.

SRIVASTANA, S.K and R. TYAGI. 1995. Competitive adsorption of substituted phenols by activated carbons developed from the fertilizer waste slurry. *Wet. Sci.* **29(2)** : 483-488

SUMMERS, R. S. and P.V. ROBERTS. 1988. Activated carbon adsorption of humic substances. I. Heterodisperse mixture and desorption. *J. Colloid Interface Sci.* **122(2)** : 367-381.